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A PRELIMINARY SURVEY OF POLYCHLORINATED BIPHENYLS (PCBs) IN AQUATIC HABITATS AND GREAT BLUE HERONS ON THE HANFORD SITE

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Pacific Northwest Laboratory Richland, Washington 99352



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SUMMARY

Polychlorinated biphenyls (PCBs), constituents of insulating fluids used in electrical transformers and capacitors, were identified during a preliminary survey of waters, sediments, and fish from five locations on the Hanford Site in southeastern Washington State: Gable Mountain Pond, B Pond, West Pond, . White Bluffs Slough on the Columbia River, and a pond on the Wahluke Slope. These aquatic areas are all within the foraging range of great blue herons (Ardea herodias) that nest on the Hanford Site.

Of those waters that contained PCBs, concentrations were found to be somewhat over 1 ng/L, but less than 20 ng/L, and equal to or less than concentrations reported for other freshwater regions of the United States. The PCBs in Sediments and fish closely resembled the chromatographic profile of Aroclor 1260, a commercial PCB mixture produced in the United States by the Monsanto \sim Company. The highest PCB concentrations were found in the upper 5-cm portions __of the Gable Mountain Pond and B Pond sediments (up to 230 ppb) and in the fat of fish from Gable Mountain Pond and White Bluffs Slough (up to 4.7 ppm). Concentrations of PCBs detected in the sediments were 10 to 100 times lower than those found in soils and sediments from other areas of the nation. Con-Centrations of PCBs in fat from Hanford great blue herons ranged from 3.6 to №10.6 ppm, while PCB concentrations in herons from other areas of the Pacific Northwest (analyzed as a part-of this study) ranged from 0.6 to 15.6 ppm. Great blue herons at Hanford contained PCB isomer distributions closely matching that of Aroclor 1260; great blue herons from other locations contained isomer distributions indicating the presence of a mixture of aroclors.

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INTRODUCTION

Polychlorinated biphenyls (PCBs) are manmade fluids that have been used in electrical transformers and capacitors associated with the industrial facilities on the U.S. Department of Energy (DOE) Hanford Site since its inception in the mid-1940's. The biological hazards of PCBs to wildlife have been well documented (Bush et al. 1974; Vos 1972; Stendell 1976; Combs and Scott 1977; Aulerich and Ringer 1977). The toxicity of PCBs to humans has been known since 1937 (Drinker, Warren and Bennett 1937). Environmental surveillance of PCBs and other toxic materials is an important function at Hanford because it provides information in support of present and future decisions concerning regulatory compliance and waste management. The chemistry and environmental chistribution of PCBs are discussed in more detail in Appendix A.

Several environmental surveillance studies have been performed that evaluate the incidence of hazardous materials in wildlife of the Hanford Site (Rickard, Hedlund and Schreckhise 1978; Fitzner, Rickard and Hines 1982). In one study, PCBs were found in the eggs of great blue herons (Ardea herodias) in concentrations ranging between 0.25 and 13.21 ppm. The origin of these PCBs is believed to be living fish that provide the primary food of great blue herons (Bent 1963).

On the Hanford Site (Figure 1), at least three different areas sustain fish that are potential food for great blue herons. These are the Columbia River, waste ponds on the Site, and seepage ponds located on the Wahluke Slope calso part of the Hanford Site, but leased to other agencies). The Columbia River supports a wide variety of fish. Waste ponds on the Hanford Site support only goldfish (Carassius auratus), but the seepage ponds support both game fish and coarse fish.

This study was prepared by Pacific Northwest Laboratory (PNL) for the DOE-Richland Operations Office to characterize the occurrence of PCBs in selected aquatic habitats on the Hanford Site and to evaluate the potential of these habitats as contributors of PCBs to nesting great blue herons. To accomplish this objective, water, sediments and fish were collected from five locations in the Hanford area and subjected to chemical analysis for PCBs. The sites

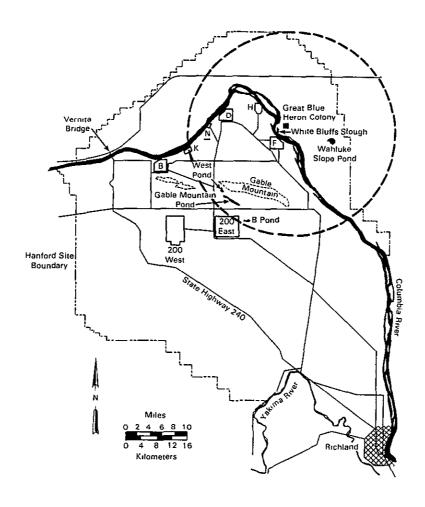


FIGURE 1. Location of Sampling Areas on the Hanford Site

examined were Gable Mountain Pond, B Pond, West Pond, White Bluffs Slough (on the Columbia River near the great blue heron colony), and an unnamed seep pond on the Wahluke Slope (Figure 1). The great blue heron colony and the basis for the selection of the sampling sites are described in Appendix B. Also the PCB chemistry of Hanford great blue herons are compared with the PCB chemistry of other great blue herons collected in the Pacific Northwest.

PCBs ON THE HANFORD SITE

Electric utility transformers, capacitors and their associated waste oils have been stored at the 212 P facility, which has been located in the 200 Area of the Hanford Site since 1981, designated as the storage facility for all PCB wastes generated by the Hanford Site. These wastes are then transported for ultimate destruction at incinerator facilities approved by the Environmental Protection Agency (EPA). In addition to the stored material, a considerable amount of PCB-containing electrical equipment is operating at locations on the Site. Laboratory analysis reports have indicated that the PCB fluids of Hanford electrical equipment consist mainly of Aroclor 1260, with smaller amounts of Aroclors 1248 and 1254. Other PCBs were disposed of at Hanford (prior to their regulation) as a result of road-oiling activities, according to

Environmental sampling has been conducted to determine the concentrations of PCBs in fish in the mainstream Columbia, Yakima and Snake rivers as part of the National Pesticide Monitoring Program (Schmitt et al. 1983). However, until the PNL survey, there were no analyses of PCBs in environmental samples from Hanford Site pond habitats, some of which have been in place since the 1950's (Rickard, Fitzner and Cushing 1981).

The water that sustains Hanford waste ponds is pumped directly from the Columbia River. The water is circulated through pipes in the industrial facilities and is mostly used as coolant. It enters the ponds as a single inlet stream at a relatively constant flow rate (Emery and McShane 1978; PRickard, Fitzner and Cushing 1981). Recent evidence indicates that one route of entry of PCBs into the waste ponds has been these inlet streams (Riley et al. 1986). The ponds have no outlet streams; water is drained by percolation to groundwater. Thus, PCBs that enter the ponds by this route eventually become incorporated into the sediments of the pond bottom.

Ponds on the Wahluke Slope are not associated with the industrial facilities on the Hanford Site. These ponds could be expected to contain PCB concentrations similar to background levels observed elsewhere in fresh waters (0.5 ppt, according to Nisbet and Sarofim 1972) and sediments (3 to 10 ppb, according to Eisenreich and Johnson 1983). Some of the Wahluke Slope ponds are

accessible to the general public and are used for sport fishing and hunting; others are used as waterfowl refuges. The waste ponds on the Hanford Site are not accessible to the general public.

PCB ACCUMULATION IN GREAT BLUE HERONS

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Although PCBs are sparingly soluble in water (Pavlou and Dexter 1979; Eisenreich and Johnson 1983), they can accumulate in fish organs and tissues (Lech and Peterson 1983; Malins et al. 1984; Gahler et al. 1982). Thus, a logical indirect pathway is present for accumulation of PCBs into such fisheating birds as great blue herons, through sediment and water, to fish, and ultimately to the bird (Figure 2).

There is only one great blue heron colony on the Hanford Site. It is located on the banks of the Columbia River, upstream from the White Bluffs ferry landing (Figure 1). Nearby colonies are located northeast of the Hanford Site, on the Potholes Reservoir in Grant County, Washington (Rickard, Hedlund and Schreckhise 1978); and southwest, at the Umatilla National Wildlife Refuge in Umatilla County, Oregon.

The waste and seepage ponds are believed to be within the foraging ranges of the great blue herons nesting on the Hanford Site, although there is no information as to how often these ponds are used by great blue herons or what percentage of their diets is derived from the waste ponds.

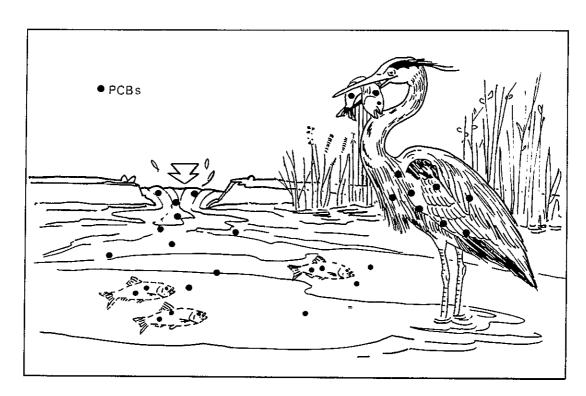


FIGURE 2. Pathway of PCB Transport from Source to Accumulation in Great Blue Herons

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RESULTS AND DISCUSSION

Sampling of water, sediment, and fish was conducted at the five study sites from December 12-16, 1983. Some samples were not collected at that time, however, because the ponds were frozen. Samples not obtained in December were collected between May 10 and June 27, 1984. Details of the sampling methods and locations of water, sediment, and birds are provided in Appendix C. The methods of chemical analysis used to determine PCB concentrations in the samples are described in Appendix D.

INVENTORY

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Table 1 summarizes the inventory data for sampling water, sediment, and fish. For sediment analysis, 10 core and two grab sediment samples were collected from each of five sites. For water analysis, two 1-L water samples were collected from each site. Trace amounts of PCBs in water were collected by passing water through two columns packed with XAD-2 resin. Volume passed through first columns ranged from 26 to 48 L, and 24 to 38 L passed through the second columns. Filtering times ranged from 4 to 6 hours. In addition, high-volume filtered water samples (approximately 500 L each) were collected at Gable Mountain Pond and West Pond.

Twenty-one fish, including largemouth and smallmouth bass, common carp, goldfish, pumpkinseed, white crappie, and bluegill, were collected by electroshocking, beach seine and lance. No fish were collected from either B Pond or West Pond, although attempts were made using the described techniques.

PCB CHEMISTRY OF WATER, SEDIMENT, AND FISH

General physical and chemical properties of the sediments are listed in Table 2. Sediments from Gable Mountain Pond and B Pond had higher average concentrations of organic matter and sulfur than sediments from the other three study locations. Both organic carbon content and sediment particle size have been shown to be important factors in interpreting the partitioning behavior of PCBs between water and sediment (Steen et al. 1978) and may be contributing factors to the observed higher concentrations of PCBs in these ponds.

TABLE 1. Inventory of Samples Collected from the Five Study Sites

Site	Date	Sample Type(a)						
Location	Sampled	Water ^(b)	Sediment (c)	Fish				
Columbia River								
White Bluffs Slough	12- 9-83 5-10-84	G(2), XAD-2(2)	C(10), G(2)	Smallmouth bass (2) Largemouth bass (2) Carp (2)				
Waste Ponds								
Gable Moun- tain Pond	12-12-83 6-26-84	G(2), XAD-2(2) HV(1)	C(10), G(2)	Goldfish (5)				
B Pond	12-13-83 6-26-84	G(2), XAD-2(2)	C(10), G(2)	None(d)				
West Pond	12-15-83	G(2), XAD-2(2),	C(10), G(2)	None ^(d)				
Wahluke Slope		HV(1)						
Unnamed Pond	12-16-83 6-27-84	G(2), XAD-2(2)	C(10), G(2)	Pumpkinseed (6) White crappie (1) Bluegill (1) Carp (2)				

(a) The number in parentheses represents samples collected.

(b) G indicates a grab sample; HV indicates a high-volume water sample; and XAD-2 indicates a resin-adsorbed water sample.

(c) C indicates a core sample; G indicates a grab sample.

(d) Although attempts were made, no fish were caught in B Pond or West Pond.

Table 3 summarizes information on the PCB content of water, sediment and fish collected from the five sites. More detailed information regarding these data can be found in Appendix E (Tables E.1 and E.2). Figures C.1 to C.5 in Appendix C identify places within each pond and slough where water and sediment samples were taken.

Concentrations in Water

Concentrations of PCBs above 20 ng/L were not detected in any of the grab samples (Table 3). Detectable levels were found in the XAD-2 samples; however,

TABLE 2. Sediment Characteristics of Five Hanford Water Bodies

	Particle Size Analysis (%)						
Location	Sample ^(a)	Water	Sand	<u>Silt</u>	<u>Clay</u>	Loss on [b]	Sulfur(b)
Gable Mountain	SG-1	53	67	32	1	5.0	0.34
Pond	SG-2	62	70	30	0	6.7	0.76
B Pond	SG-1	55	81	18	1	4.4	0.20
	SG-2	56	66	33	1	7.4	0.60
West Pond	SG-1	42	83	14	3	3.2	0.11
	SG-2	27	79	18	3	1.2	0.09
White Bluffs Slough (Columbia River)	SG-1	33	88	9	3	2.7	0.06
Wahluke Slope	SG-1	24	95	4	1	1.0	0.08
(Unnamed pond)	SG-2	49	69	28	3	5.4	0.26

⁽a) SG indicates a sediment grab sample--locations are shown in Figure 4.

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These data suggest that PCB levels in waters of Gable Mountain Pond,

B Pond, and the Columbia River at White Bluffs Slough are somewhat over 1 ng/L,
but less than 20 ng/L. This hypothesis is substantiated by the data obtained
from the high-volume filter samples (Table 3) and indicates that the concentrations are equal to or less than concentrations reported for other freshwater
regions of the United States (Pavlou and Dexter 1979; Nisbet and Sarofim 1972).

While the filter samples results from Gable Mountain Pond are in agreement with the XAD-2 data, the filtration results from West Pond are more than an order of magnitude higher than those from the XAD-2 data. No PCBs were expected in XAD-2 and filter samples at the West Pond since concentrations in

⁽b) Measurements are based on dry weight.

there was poor reproducibility between duplicate samples. For example, the samples from Gable Mountain Pond were 1.9 ng/L in one replicate and not detectable in the other, and similar results were obtained in samples from White Bluffs Slough.

TABLE 3. Ranges of PCB Concentrations in Water, Sediment, and Fish Collected from Five Study Sites

Sample Type	White Bluffs Slough (Columbia <u>River)</u>	Gable Mountain Pond	B Pond	West Pond	Wahluke Slope (Unnamed Pond)
Water ^(a) Grab XAD-2 High Volume	<20 <0.04-2.76 NC (d)	<20 <0.3-1.9 0.9	<20 1.39-3.75 NC	<20 <0.3-0.4 10.1	<20 <0.5 NC
Sediments(b) 0-5 cm 5-10 cm	_{ND} (e) ND	1-130 ND-26	6-230 6-220	ND -4 <1-1	ND -2 ND -<1
Fish ^(c) Liver Eggs Fat Gonads	<0.04-0.16 <0.04-0.44 4.72 <0.04	<0.4-2.4 <0.4 2.09-4.40 NA(†)	NC NC NC NC	NC NC NC NC	<0.04 <0.04 <0.04 <0.04

⁽a) ng/L. For further information on the water data, see Table E.1 of Appendix E.

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sediments from West Pond were either not detectable or very low. The filtration results suggest that additional sampling of West Pond would reveal sediment that contained higher PCB concentrations. Additional sampling of water and sediments is needed to verify these suggested findings. These data also suggest that sampling of a water body by high-volume filtration may be useful for determining whether sediments of a water body are contaminated by PCBs. The effort required for determining the extent of sediment contamination in a water body could be reduced if a positive correlation could be demonstrated between concentrations of PCBs in suspended matter and in sediment.

⁽b) $\mu g/Kg$. For further information on the sediment data, see Table E.2 of Appendix E.

⁽c) $\mu g/Kg$. For further information on the fish data, see Table E.3 of Appendix E.

⁽d) NC indicates that no sample was collected.

⁽e) ND indicates that no PCBs were detected.

⁽f) NA indicates that no analysis was made.

Concentrations in Sediment

All PCBs found in the analyzed sediments (Table 3) fit the chromatographic profile of Aroclor 1260, and no evidence for the presence of other aroclors was indicated. In addition to PCBs, other electron-capturing compounds were found to be present in many of the samples that were not present in blanks. These were not investigated further; it is likely that some could be insecticide or herbicide residues.

Highest concentrations of PCBs were found in the sediments from B Pond. Concentrations of about 200 $\mu g/kg$ were found in samples from close to the pond inlets, and also at the deepest point (Figure C.3). The range of PCB concentrations in the upper 5 cm was 6-230 $\mu g/kg$, and the average was 116 $\mu g/kg$. Because of the limited number of samples, it is not possible at this time to draw conclusions about the origin of the PCBs in B Pond.

Sediments from Gable Mountain Pond were also found to contain PCBs, although concentrations were generally lower than those found in sediments from B Pond. Again, highest concentrations were found in sediment samples near the inlet (Figure C.2). Samples in the upper 5 cm yielded an average Aroclor 1260 concentration of 28 μ g/kg; range, 0 to 148 μ g/kg. PCB concentrations in samples taken near a road crossing the pond were not particularly high, which would suggest that the principal source of contamination of the pond was through the waste-water inlet to the pond. This conclusion is supported by a more rigorous study conducted on Gable Mountain Pond prior to its decommissioning (Riley et al. 1986).

Analysis of sediments from other locations shows no evidence of significant PCB contamination. No detectable concentrations of PCBs were found in any of the sediment samples from the White Bluffs Slough of the Columbia River, and only traces of these components were found in some sediments of the Wahluke Slope pond and West Pond. Additional sampling of those sites is needed to verify these suggested findings.

Concentrations in Fish

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Fish were obtained at three locations: Gable Mountain Pond, White Bluffs Slough, and a pond on the Wahluke Slope. These locations represent.

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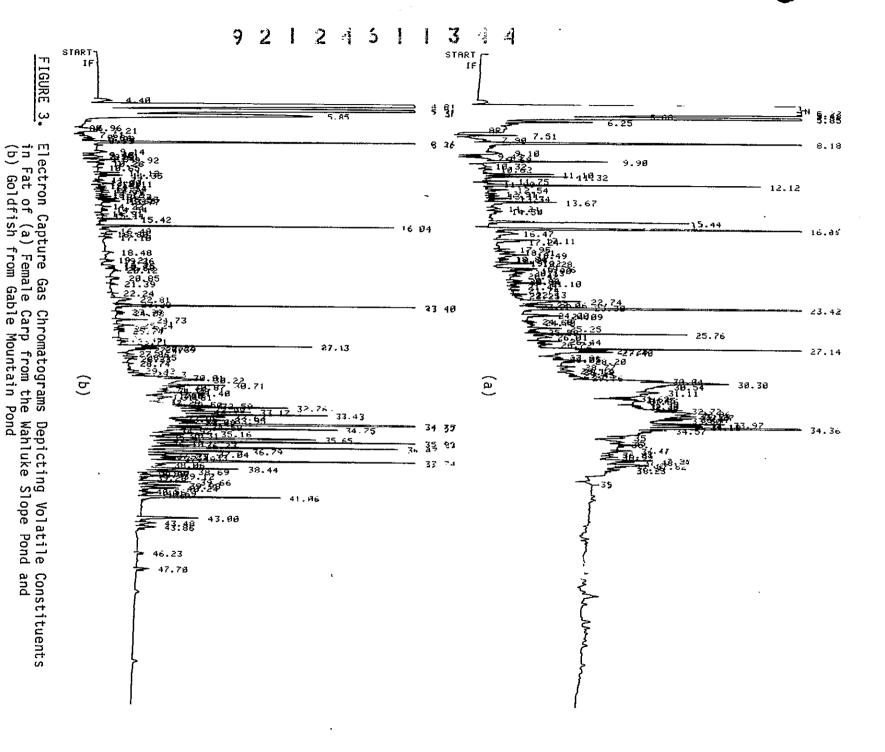
respectively, a site known to be contaminated by PCBs, a site subject to a variety of contaminant inputs, and a site not believed to have been exposed to any PCB contamination. The results based on our sampling are consistent with these assumptions: PCBs were not measurable in fish from the Wahluke Slope site, but they were found in fish from the other two sites (Table 3). Gas chromatograms from the Wahluke Slope pond and Gable Mountain Pond fish samples are compared in Figure 3.

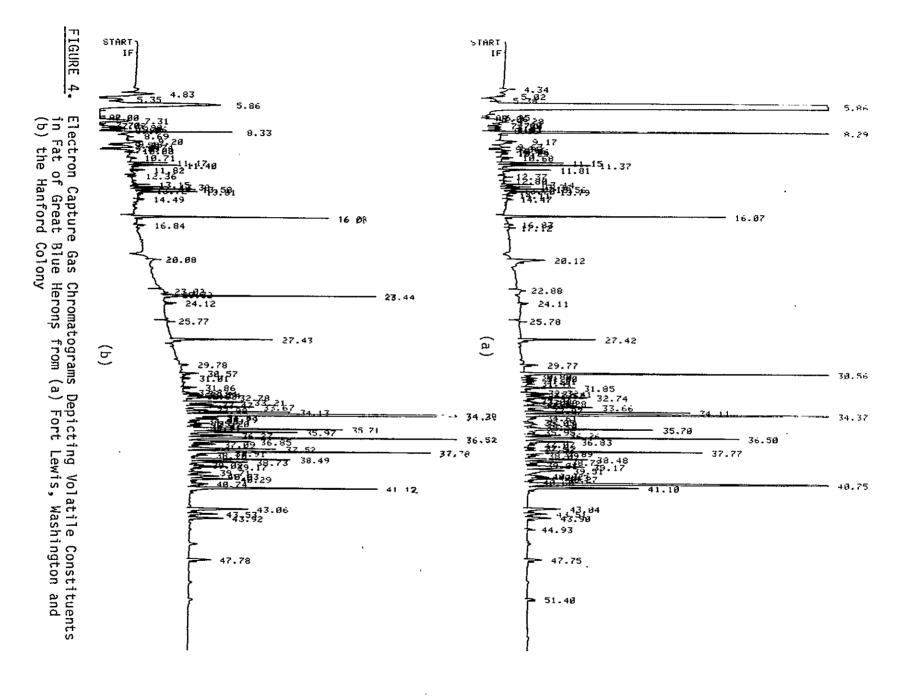
All PCB chromatograms obtained from the samples closely resembled the chromatographic pattern of Aroclor 1260. The highest concentrations of PCBs were found in the body fat. The generally low levels found in eggs and gonads are somewhat surprising, since these are relatively high in lipid content and were thought to be good candidates for adsorbing lipophilic PCBs. Significant concentrations of PCBs in eggs were only found in one fish from White Bluffs Slough. Only one fish from Gable Mountain Pond and two from White Bluffs Slough had liver PCB concentrations in excess of 0.1 μ g/g.

The concentration of PCBs found in fish from the Hanford Site are consistent with those found in fish taken from the Columbia River near Pasco, Washington (about 67 km down river), between 1976 and 1978 (Schmitt et al. 1983), although more Aroclor 1254 was found in the Pasco fish than Aroclor 1260. Concentrations reported for whole fish in our study were between 0.0 and 0.33 μ g/g. The highest concentration of Aroclor 1260 found in Schmitt's samples was 0.2 μ /g. Our data base suggests a correlation between PCB concentrations in the fatty tissues of fish from Gable Mountain Pond and those in fish from the Columbia River (3.2 \pm 0.9, n = 5 vs. 4.7, n = 1); however, more data are needed to confirm this relationship, since only one fish from the Columbia River had sufficient fat to analyze for PCBs.

PCB CONCENTRATIONS IN GREAT BLUE HERONS

Inspection of the gas chromatograms obtained from Hanford juvenile great blue herons indicated substantial differences in the tissue chemistry between these birds and those from other areas of the Pacific Northwest (Figure 4). The Hanford birds contained PCB isomer distributions closely matching Aroclor 1260. The chromatograms from non-Hanford birds contained additional peaks, as well as isomer distributions indicating the presence of a mixture of aroclors.





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The pattern obtained from those birds did not match any aroclor standard, which suggests that the Hanford birds may have obtained PCBs from a diet local to the Hanford Site, a diet that could include fish from the Aroclor 1260-contaminated waste ponds in the 200 Area and the Columbia River. More rigorous sampling and analysis of samples from these locations as well as additional ponds within the area are required to confirm this conclusion.

The results of the analyses of tissues from great blue herons taken from the Hanford Site and from other Pacific Northwest regions are shown in Table 4. For the most part, analyzed samples consisted of fat. The samples designated "proventricular" were dissected from the proventriculus tissues. Samples of fat were also taken from other places in the body.

Average concentration in Hanford bird fat (body/proventricular) for four birds was 7.2 and 6.0 $\mu g/g$, respectively. The average PCB concentration ranged from 2.7 to 3.0 $\mu g/g$ for birds from Fort Lewis, Washington, to 6.2 to 15.6 $\mu g/g$ for birds from Chatcolet, Idaho. The limited sample size prevents a discussion of concentration similarities and differences among the three sites.

TABLE 4. Concentrations ($\mu g/kg$) of PCBs in Fatty Tissues of Juvenile Herons from the Hanford Site and Other Locations in the Pacific Northwest, 1982

04	Hanford Site, Wash.			Lewis, Wash.	Chatcolet, Ida.		
war-ann	Body	Proventricular	Body	Proventricular	Body	Proventricular	
2	3.6	(a)	0.8	5.4	15.6	6.4	
o-	7.6 10.6	6.5 5.5	4.6 	0.6	NB(b)	6.0 NB	
	6.9	->	NB	NB	NB	NB	
Averag	ge 7 . 2	6.0	2.7	3.0	15.6	6.2	

⁽a) Dash indicates that sample was not collected because of insufficient tissue.

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⁽b) NB indicates that no bird was collected.

CONCLUSIONS

The conclusions listed below are based on a limited sampling of Hanford aquatic habitats. However, these conclusions are worthy of notice and verification.

Concentrations of PCBs were detected in waters collected from Gable Mountain Pond, B Pond, West Pond, and the Columbia River at White Bluffs (White Bluffs Slough), but not from the Wahluke Slope. Data obtained on the basis of three independent sampling methods suggest that PCB levels in the waters of Gable Mountain Pond, B Pond and White Bluffs Slough are somewhat over 1 ng/L but less than 20 ng/L. This concentration range was equal to or less than concentrations reported for other freshwater regions of the United States.

PCBs were detected in sediments of Gable Mountain Pond, B Pond, West Pond and an unnamed pond on the Wahluke Slope, but not in the White Bluffs Slough. The highest concentrations were observed in Gable Mountain and B Ponds. Only trace amounts were detected in West Pond and the Wahluke Slope pond. Concentrations ranged from not-detected (detection limit 0.1 ppb) to 230 ppb and were 10 to 100 times lower than PCB concentrations detected in soils and sediments from other areas of the nation. Sediment PCBs fit the chromatographic profile of Aroclor 1260.

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PCBs were detected in the tissue of fish collected from the White Bluffs Slough and Gable Mountain Pond, but not in fish from the pond on the Wahluke Slope. Concentrations ranged from not-detected (<0.04 ppm) to 4.72 ppm. Fish PCBs closely resembled the chromatographic profile of Aroclor 1260.

Great blue herons nesting on the Hanford Site contained PCB isomer distributions closely matching that of Aroclor 1260; non-Hanford birds contained isomer distributions indicating a mixture of aroclors. Concentrations of PCBs in Hanford birds ranged from 6.0 to 7.2 ppm. Concentrations in non-Hanford birds ranged from 2.7 to 15.6 ppm.

APPENDIX A

PCB CHEMISTRY AND ENVIRONMENTAL DISTRIBUTION

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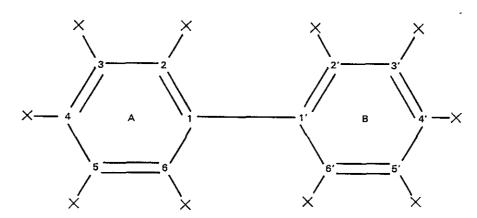
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PCB CHEMISTRY AND ENVIRONMENTAL DISTRIBUTION

CHEMICAL CHARACTERISTICS AND INDUSTRIAL FORM OF PCBs

Polychlorinated biphenyls (Figure A.1) represent a class of manmade chlorinated aromatic hydrocarbons that are thermally and chemically very stable. Specifically, PCBs are a mixture of specific biphenyl hydrocarbons with varying degrees of chlorination. Substitution by chlorine on the ring structure of biphenyl gives rise to 209 possible chlorobiphenyl isomers. In commercial preparations, mixtures of chlorobiphenyls are usually present rather than any single, pure compound. The Monsanto Company (St. Louis, Missouri) has been the largest producer of PCBs in the United States and the United Kingdom, and has assigned the trade name "Aroclor" followed by a 4-digit number. The first two digits of this number indicate the type of mixture, and the last two digits represent the approximate weight percentage of chlorine in the product (Table A.1). Detailed physical and chemical properties of individual PCBs and their commercially available technical mixtures have been compiled by



1 - 6 Carbon Atoms in Aromatic Ring A

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1' - 6' Carbon Atoms in Aromatic Ring B

X H or CI, Depending on Chlorination

FIGURE A.1. Biphenyl Structure and Number of Carbon Atoms in Each Ring (Pal, Weber and Overcash 1980)

TABLE A.1. Approximate Composition of the Commercially Available Aroclors (Pal, Weber and Overcash 1980)

Empirical				Aroclor							
Formula	Chlorine Atoms	Isomers	Weight	Chlorine	1221	1232	1242	1248	1254	1260	1016
$^{\rm C}_{12}{}^{\rm H}_{10}$	0	1	154	0	11	<0.1	<0.1		<0.1	600-600	<0.1
с ₁₂ н ₉ с1	1	3	189	18.8	51	31	1		<0.1		1.0
$C_{12}H_8C1_2$	2	12	223	31.8	32	24	16	2	0.5		20
с ₁₂ н ₇ с1 ₃	3	24	258	41.3	4	28	49	18	1.0		57
с ₁₂ н ₆ ст ₄	4	42	292	48.6	2	12	25	40	21		21
с ₁₂ н ₅ ст ₅	5	46	326	54.3	<0.5	4	8	36	48	12	<0.1
$^{\mathrm{C}}_{12}^{\mathrm{H}_{4}^{\mathrm{C1}}_{6}}$	6	42	361	58.9		<0.1		4 .	23	38	
с ₁₂ н ₃ ст ₇	7	24	395	62.8			<0.1		6	41	
$c_{12}H_2c1_8$	8	12.	430	66						8	
$C_{12}H_1C1_9$.	9	3	464	68.7						1	
Average Mo	lecular Weight				201	232	267	300	328	376	258

Hutzinger, Safe and Vitko (1974). PCB oils can also contain trace quantities (ppm level) of highly toxic polychlorinated dibenzofurans (PCDFs). These compounds have been identified in commercial PCB preparations at concentrations ranging from 1 to 20 ppm. Fires in electrical transformers and capacitors containing PCB fluids have also resulted in PCDF formation (Vuceta et al. 1983).

DISTRIBUTION OF PCBs IN THE ENVIRONMENT

Introduction of PCBs into the environment was initiated with their mass-scale manufacture and use (since 1930) as insulating fluids of electrical transformers and capacitors, and as fire retardants. There are several potential routes into soils, sediments, and surface waters:

- leaks from sealed transformers and heat exchangers
- leaks of PCB-containing fluids from hydraulic systems that are only partially sealed
- spills and losses in the manufacturing of either PCBs or PCBcontaining fluids
- vaporization or leaching from PCB-containing formulations
- disposal of waste PCBs or PCB-containing fluids.
- The most likely route into the atmosphere is through incineration of PCB-containing wastes. As a result of these routes of entry, it is speculated that PCBs are now of worldwide distribution. Like pesticides, they tend to accumulate in food chains from contaminated water, sediment and soil. The PCBs introduced into various North American environments amount to roughly 3.5 x 10^6 tons, of which 3 x 10^5 tons are disposed to landfills. The remaining PCBs are associated with sediments of lakes and rivers, and are widely distributed over land and water through aerial fallout and spills (Nisbet and Sarofim 1972).

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APPENDIX B

THE GREAT BLUE HERON COLONY: BACKGROUND INFORMATION AND BASIS FOR SELECTION OF STUDY SITES

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APPENDIX B

THE GREAT BLUE HERON COLONY: BACKGROUND INFORMATION AND BASIS FOR SELECTION OF STUDY SITES

The great blue heron (<u>Ardea herodias</u>) is a large, fish-eating bird that characteristically nests in trees. One to a dozen or more nests can be constructed in a single tree. On the Hanford Site, about 50 active great blue heron nests are established each year in a small grove of tall trees located on the western shore of the Columbia River near the abandoned White Bluffs ferry landing.

Nest-building usually begins in April, and young birds are in the nests from May through July. Parent birds forage daily for fish to feed the growing young. During this season of the year, the parent birds have several potential sources of fish. The Columbia River contains a large fish population and is probably the source of most of the great blue heron foods. However, fish are also present in the waste ponds in the 200 Areas, located 8 km west of the great blue heron colony; and in the ponds on the Wahluke Slope, located east of the heron colony at about the same distance.

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During the nesting season, great blue herons are confined to their smallest travel distances because they must return to the nest at frequent intervals to feed the young birds. Thus, any chemical contaminants detected in heron fecal materials or the fish scraps cast from the nests, and any PCBs in the bodies of juveniles, have probably been gathered from a relatively small foraging zone. The sizes of the individual foraging zones are not actually known, but it is reasonable to expect that the parent birds forage consistently in one area and that juveniles from different colonies would receive fish with different kinds and amounts of chemical contamination. On the basis of this supposition, in order to obtain a representative collection, birds were sampled from colonies located both near and far from known sources of PCBs.

APPENDIX C

SAMPLING METHODS AND LOCATIONS

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APPENDIX C

SAMPLING METHODS AND LOCATIONS

COLLECTION OF WATER

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Bulk water (grab samples) and two types of filtered water were collected. Filtered samples consisted of 1) water being passed through a high-volume system (Gable Mountain Pond and West Pond only); and 2) water being passed through XAD-2 resin columns (all sites).

Bottled (Bulk) Water Samples

One-liter samples of water were collected directly from each pond and placed in polyethylene bottles. The bottles were capped, marked with an identifying code, and placed on ice for transport to the laboratory.

High-Volume Filtered Samples

A large high-volume sampler was used to filter about 500 L of water (Silker et al. 1971). The water was pumped directly from the pond and through the filter system. The filters were 30 cm in diameter and arranged in parallel within the system. Only the filtrate was saved for the analysis of PCBs on suspended matter.

XAD-2 Resin Samples

Water was pumped through duplicate 2.5 x 22.9-cm stainless steel columns filled with XAD-2 resin (Bean 1983). The water was pumped directly from the ponds through the columns, and filtrate was collected in 110-L plastic cans. Water flow was adjusted to about 80 mL/minute for each column. Total volume collected was estimated by measuring the water collected in the cans. After pumping was completed, the columns were removed from the pump, capped, marked with an identifying code, and placed on ice for transport to the laboratory.

COLLECTION OF SEDIMENTS

Sediment samples consisted of 10 core samples and 2 grab samples from each site. Samples were collected from areas where sediment was at least 10 cm deep and where there were no rocks or areas overgrown with aquatic vegetation. Other areas considered were those near the edge of the pond or at the end of a road. In some cases, areas near pond inlets were also sampled.

Grab Samples

Grab samples were collected at all sites and consisted of scraping (by hand) 2.5 to 5.0 cm of sediment, from an area approximately 30 cm square, into a 1-L glass jar. In the field, samples were kept frozen in ice chests, covered with dry ice, then transported to the laboratory, where they were stored in a freezer at -20°C.

Core Samples

Core samples were collected in PVC pipe sections 10 cm deep and 12.7 cm in diameter. The pipe was beveled at one end to provide a cutting edge for easier insertion into the sediment. Each pipe section was fitted with two PVC pipe caps (one at each open end).

Cores were collected by pushing the pipe section 10 cm into the sediment, beveled end down. The pipe was then hand-excavated and undermined; the caps were placed on the bottom and top. In areas where the pond was too deep to wade (more than 61 cm), cores were collected by scuba divers. Pipe insertion and hand excavation were the same whether accomplished by diver or wader.

Cores were transported to the surface by hand to ensure that they were upright. The caps were secured to the pipe sections, and the sample code was written on the section. All samples were marked with arrows designating the bottom and top of the sample, date collected, and sample designation. Sample codes were recorded in lab books.

Samples were placed in ice chests and covered with dry ice, to be kept frozen in the field for transport to the laboratory. There, they were stored in a freezer at -20° C.

COLLECTION OF FISH

Electroshock, beach seine and lance were used to collect fish from Gable Mountain Pond, a pond on the Wahluke Slope and White Bluffs Slough, the sites where fish were available. The variety of methods was necessary because of the range of aquatic habitats represented by the ponds. Sampling was concentrated along shorelines suspected as bird foraging areas. At each site, a systematic search of the shoreline and other areas was conducted to collect whatever fish were available. At those sites where fish were present, three to five fish were collected.

As samples were collected, they were marked with the date, sample location, and sample type. Samples were placed in ice chests and covered with dry ice. They were kept frozen in the field and transported to the laboratory on ice. They were then stored at -20° C.

COLLECTION OF BIRDS

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Great blue herons (about 5 weeks old) were collected from the Hanford Site; the Fort Lewis Military Reservation, near Tacoma, Washington; and near Lake Chatcolet, Idaho, in 1982. All of the juvenile herons and eggs were collected in cooperation with Dr. Lawrence Blus of the U.S. Fish and Wildlife Service, Corvallis, Oregon. The birds were stored in the laboratory at -60°C.

SAMPLING LOCATIONS

Figures C.1 through C.5 provide detail (not to scale) of the five sampling locations: White Bluffs Slough, Gable Mountain Pond, B Pond, West Pond, and the Wahluke Slope pond.

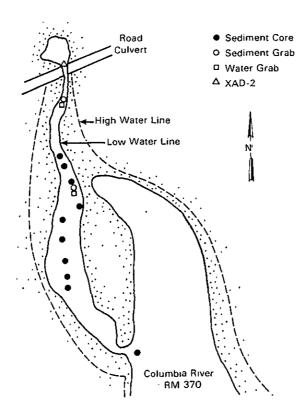


FIGURE C.1. Sampling Locations in White Bluffs Slough

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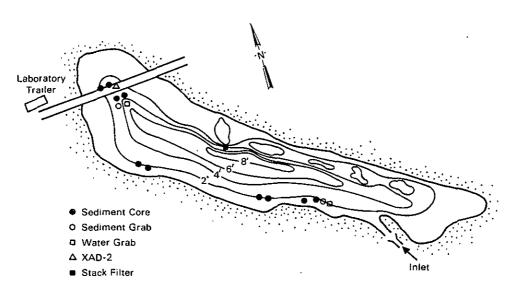


FIGURE C.2. Sampling Locations in Gable Mountain Pond

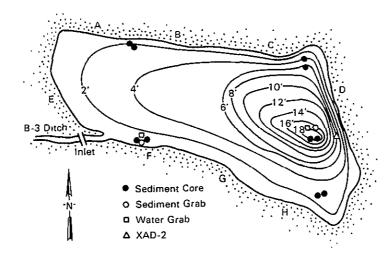
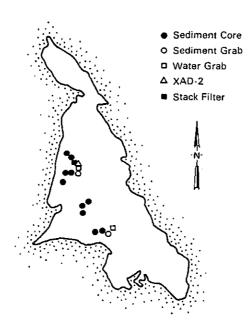


FIGURE C.3. Sampling Locations in B Pond



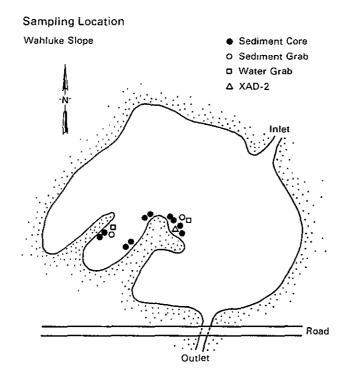


FIGURE C.5. Sampling Locations in a Pond on the Wahluke Slope

REFERENCES

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APPENDIX D

ANALYTICAL METHODS

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APPENDIX D

ANALYTICAL METHODS

WATER

Because PCBs have very low solubility in water, three sampling methods were used. Grab samples are easy to collect and simple to analyze, but do not permit highly sensitive analysis because they are small. High-volume filtration requires substantially more effort for sampling and analysis, but permits much higher sensitivity because of the large sample. Adsorption of trace levels of organics from water onto XAD-2 resin represents an intermediate level of effort and sensitivity. Experience demonstrated that use of the more sensitive methods was essential to obtain reliable information about PCB concentrations in the ponds studied.

Grab Samples

The water sample was carefully poured into a 1-L separatory funnel, several drops of 50% sulfuric acid were added, and the sample was extracted twice with 25 mL methylene chloride. The combined solvent extracts were dried over anhydrous sodium sulfate, and evaporated into 1 mL n-heptane under a stream of dry nitrogen. The heptane sample was then directly analyzed in the gas chromatograph as described below for sediment analysis. Recovery of samples spiked with Aroclor 1260 (3.12 mg, added in 1 mL acetone) was 113 ± 7%.

As a further check on the analysis, a standard Aroclor 1254 sample was obtained from the U.S. Environmental Protection Agency (EPA) and analyzed using the procedure described above. The results (2.92 \pm 0.29 μ g/L) were well within the range given (2.9 μ g/L; acceptable range, 1.1 - 3.9 μ g/L).

Analysis of Suspended Matter Collected on High-Volume Filters

Individual filters were placed in a Soxhlet cup and extracted in a Soxhlet extractor for 24 hours with benzene/methanol. The extracts were then treated as if they were sediment samples (i.e., mercury and silica gel cleanup, followed by gas chromatography as described for sediment analysis). Since each

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filter collected one-eighth of the total water sample (filtration was in parallel), the results for each filter were multiplied by 8 to express the results in micrograms per liter.

Water Adsorbed on XAD-2 Columns

The XAD-2 samples were eluted with 200 mL diethyl ether over a period of 30 minutes. Water, which also eluted from the column during extraction, was removed with a pipette, and the ether extract was dried overnight over anhydrous sodium sulfate. Then the extract was reduced by rotary evaporation to about 2 mL, transferred to a soluvial, and brought to 1 mL in n-heptane under a stream of nitrogen. The sample was further purified by mercury removal of sulfur, and by silica gel percolation (as described for sediment analysis later in this appendix). Gas chromatographic analysis and quantification of the sample were performed on the purified sample (also as described for sediment analysis).

SEDIMENT

Sediment Subsampling

Subsamples of sediment that were analyzed for PCBs were sent to a commercial laboratory for determination of particle size, water content, sulfur, and weight loss on ignition at 550°C. Loss on ignition is a reflection of the organic matter content of the sediment sample.

Sediment cores were subsampled by immersing the frozen core and casing in tap water for 15 minutes. This permitted the core to be extruded from the casing while still frozen solid. The core was cut into two 5-cm sections by means of a diamond-tipped circular saw used for cutting large glassware. Each depth section was further cut in half to provide duplicates for each core at each depth. For the analysis, one of the duplicates of the top half was thawed, mixed, and a 100-g subsample taken.

Extraction and Cleanup of Sediments

The procedures used to extract and concentrate the samples and remove interfering material are summarized in the flow diagram of Figure D.1. A number of EPA studies were reviewed prior to selection of the method used for

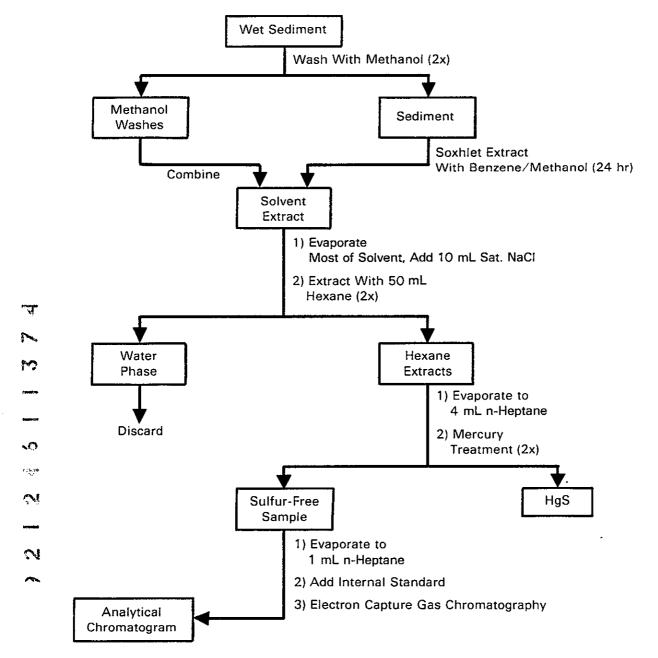


FIGURE D.1. Scheme for the Preparation of Sediments for Chemical Analysis

PCB analysis (Caragay and Levins 1979; Rodriguez, McMahon, and Thomas 1980; Hern, Lambou, and Tai 1979). In addition, the FDA Pesticide Analytical Manual (U.S. FDA 1977) was consulted, particularly for extraction and concentration procedures. The method also borrows heavily from those previously used in PNL

laboratories during the conduct of sediment analysis programs for NOAA and DOE (Riley, Thomas, and Bean 1979; Riley et al. 1980, 1981, 1984).

Sediment Extraction

A 100-g sample of wet sediment was weighed into a 200-mL glass centrifuge bottle, stirred with methanol (50 mL), and centrifuged at 163 x gravity for 10 minutes. The methanol supernatant was removed and saved. The methanol wash was repeated, the supernatants from the two sequences were combined, and the mixture was poured through glass wool to remove any mineral residue. The glass wool was rinsed with an additional 10 mL methanol, which was also combined with the methanol washes. Benzene (2 mL) was added to ensure that the PCBs in the wash stayed in solution. The methanol washes were then set aside.

The washed sediment was transferred to a weighed Soxhlet thimble (medium frit) and extracted in a Soxhlet apparatus for 48 hours with a mixture of 180 mL benzene and 120 mL methanol. Then the Soxhlet cup was removed, and the material was allowed to dry in the hood for 24 hours, dried further in a forced-air oven at 100°C, and weighed to obtain the weight of the dry sediment.

The benzene/methanol extract was poured through glass wool to remove any mineral particles. The wool was rinsed with benzene (10 mL) and the rinse combined with the extract; then the extract was evaporated in a rotary evaporator until about 20 mL of the organic phase remained. The methanol washes were added to this material, using three 5-mL washes of hexane to transfer. Evaporation was continued to, again, about 20 mL organic phase. N-heptane was added (4 mL) and the evaporation continued until volume was reduced to 4 mL organic phase. The heptane addition and evaporation process was repeated once to ensure removal of methanol.

The evaporation residue was transferred to a 250-mL separatory funnel with 50 mL hexane. Saturated aqueous NaCl (10 mL) was added, the funnel was shaken for 1 minute, and the hexane was removed. The hexane extraction was repeated, and the extracts were combined and dried over anhydrous $\rm Na_2SO_4$. The dried extract was reduced to about 6 mL with the roto-evaporator and transferred to 5-mL soluvials. Volume was then reduced to 4 mL under dry nitrogen.

Sulfur Removal

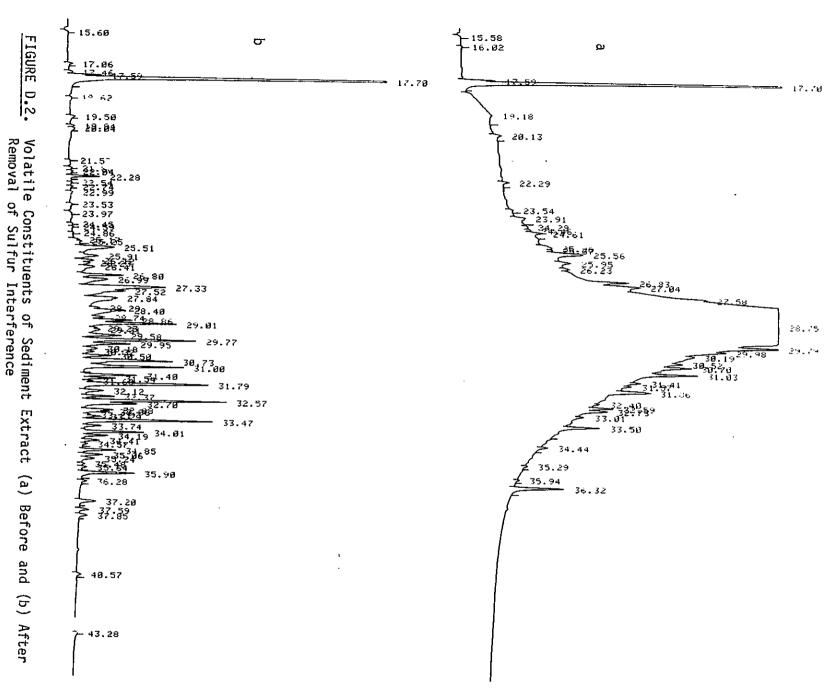
Elemental sulfur was a major contaminant in almost all samples analyzed. It was necessary to remove sulfur from the samples because it is sufficiently volatile to emerge from the gas chromatography column, and it exhibits a significant response in the electron capture detector used for the analysis of PCBs. Further, sulfur appears in the chromatogram at about the same retention time as the PCBs.

Metallic mercury (USP) was used to remove sulfur according to the procedure of Caragay and Levins (1979). Prior to use, the mercury was treated with concentrated nitric acid, then washed with distilled water followed by methanol, and dried under a stream of nitrogen. Six small drops (ca. 5 g) of mercury were added to each sample (in soluvials, after extraction and concentration). Then the samples were vigorously agitated in a test tube vortex mixer for 20 minutes. The treated heptane solution was then transferred to a remove all interfering sulfur, and the sample was ready for further cleanup over silica gel. Chromatograms depicting the effectiveness of the treatment of removal of sulfur from the sediment extracts are shown in Figure D.2.

Silica Gel Cleanup

Constituents in the mercury-treated samples were separated by chromato-—graphy over silica gel using a previously reported procedure (Warner 1976). At PNL, it has been used for some time as a general technique for cleanup of aromatic organics in environmental samples.

Fifteen grams of 100 to 200-mesh silica gel, activated at a temperature of 150°C overnight, was slurry-packed into a 25 x 25-cm glass column using hexane. The column content was cleaned by passing successively 30 mL methylene chloride and 40 mL hexane through the column. The sample, reduced to 1 mL n-heptane, was placed on the column, and the column eluted first with 40 mL hexane, then 86 mL methylene chloride. The bulk of the solvent in the fraction eluted with methylene chloride and containing the PCBs was removed by rotary evaporation. N-heptane was added, and the remaining solvent was removed under a stream of nitrogen. Final volume was 1 mL.



D.6

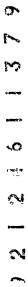
<u>Gas Chromatographic Analysis</u>

Prior to analysis by gas chromatography, 10 μ L of an internal standard was added by syringe to the sample contained in 1 mL n-heptane. The internal standard was 1-bromonaphthalene, prepared by adding 50 μ L to 50 mL n-heptane, followed by a further 1:25 dilution in n-heptane. After shaking, the sample was ready for analysis. Aroclor standards used for comparison were also treated with internal standard prior to chromatography.

Analysis was performed on a Hewlett-Packard Model 5840 gas chromatograph (Hewlett-Packard Co., Avondale, Pennsylvania), using a capillary injector in the splitless mode. The capillary chromatography column used for separation was 60 m long. Column conditions were as follows: helium flow, 2 mL/minute; initial temperature, 70°C; hold for 2 minutes, then 6°C/minute to 250°C, and hold for 20 minutes. Detection was by electron capture detector operated with 40 mL/min flow of 10% methane in argon.

Because of interference by other electron-capturing peaks, quantification of PCBs by integrating all peaks in the region of PCB retention time was not appropriate. We found that good results could be obtained by selecting nine prominent peaks and comparing their total area to the corresponding nine peaks an an Aroclor 1260 standard. The peaks selected for quantification are shown in the chromatogram of Figure D.3. At times, interfering peaks would mask the peaks selected for quantification. In that case, quantification was based on those peaks not masked, and they were compared with the corresponding peaks in the standard.

Efficiency of recovery was checked by spiking 3.12 μg Aroclor 1260 into sediment samples known to contain elemental sulfur, but not containing appreciable quantities of PCBs. Recovery from triplicate spiked samples was 3.44 \pm 0.01 μg , or 110%. The reason for the high recovery is not known, but the results are quite adequate for the analytical study.



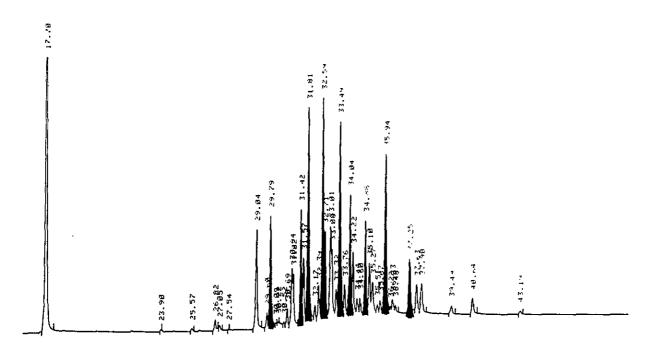


FIGURE D.3. Peaks (Darkened Areas) Used for the Quantification of Total PCBs in Environmental Samples

FISH AND BIRD TISSUE

<u>Dissection of Fish Tissue</u>

Fish collected from White Bluffs Slough, the Wahluke Slope pond, and Gable Mountain Pond were thawed at room temperature overnight and subsequently subjected to dissection. All or part of the liver, gonads (eggs), and visceral fat was removed from each fish. Approximately 2 g of each sample was placed in tared scintillation vials, and stored at -70°C until chemical analysis was performed. Thirteen fish were dissected, representing six species.

Bird Necropsy

Great blue herons collected in the field were returned to the laboratory and stored at -60°C. Prior to necropsy, the birds were thawed overnight at room temperature. During necropsy, the sex, age, and general state of health of each bird were noted. Duplicate samples of muscle, fat, liver, and bone tissue, as well as the kidneys, brain, and genitalia, were excised for PCB residue and archived. Most of the primary feathers were also removed and archived. In addition to the liver from one heron, only fat samples were used

for PCB analysis; the remaining tissues were archived. Fat was removed from two general locations: the exterior of the proventriculus and from several locations outside of the body cavity (e.g., along the sternum and inside the thighs). Approximately 2 g of the excised fat was then placed into previously tared Teflon®-lined scintillation vials and stored at -60°C until chemical analysis was performed.

Tissue Digestion, Extraction and Cleanup

The method used for extraction and cleanup of both fish and bird tissues was adapted from the procedure described by Warner (1976). Although this technique was originally developed for the analysis of relatively inert aliphatic and aromatic hydrocarbons, tests performed showed that few, if any, losses of PCBs or changes in distribution of PCB isomers were brought about by the analytical conditions employed.

Approximately 2 g tissue, obtained by careful dissection of a bird or fish, was weighed into a 22-mL scintillation vial with a Teflon®-lined cap.

For samples of fish, 1 mL 5N NaOH was added; for bird tissue, 5 mL 5N NaOH was added. The samples were then heated at 90°C for 1 hour. When they had cooled, 10 µL of a hexane solution containing 1.36 µg of 1,2,3-trichlorobenzene was added for use as an extraction recovery standard. The sample was then shaken with 1 mL n-heptane for 1 minute and heated for 10 minutes at 80°C to break the resulting emulsion. Occasionally, centrifugation was also required to demulsify the sample. The heptane solution was then removed by pipette to a clean soluvial prior to cleanup by silica gel. The silica gel cleanup procedure used for tissue samples was identical to that used for sediments.

Gas Chromatographic Analysis

To the methylene chloride fraction from the silica gel procedure, now in 1 mL n-heptane, was added 10 μ L of a solution of 1-bromonaphthalene as analytical internal standard. After shaking, 1 μ L was injected into the gas chromatograph. Electron capture gas chromatography was performed with a Hewlett-Packard 5840 instrument fitted with a capillary column 60 m x 25 mm, using a

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sample splitter at a split ratio of 10:1. At injection, the temperature was held at 70°C for 4 minutes, followed by an 8°C/minute program rate to 280°C , and that temperature was held for 30 minutes.

Quantitative analysis was accomplished by comparing peak areas in sample chromatograms with those obtained from standard heptane solutions containing 1.95 µg Aroclor 1260 and the quantities of extraction recovery and analytical standards added to tissue samples. The nine-peak quantification method employed for sediment samples (Appendix D) was also used for tissues. Quantification of PCBs in samples was performed using the trichlorobenzene extraction recovery standard as an analytical internal standard.

Although extraction efficiency from the tissue samples was only fair (ca. 50%; range, 25-80%), use of the trichlorobenzene recovery standard as internal standard automatically compensated for these losses. Analysis of tissue samples spiked with 1.95 μ g of Aroclor 1260 gave overall recoveries of 128 \pm 6%. The high recoveries are believed to result from preferential evaporation of trichlorobenzene during the sample concentration step. Reproducibility of analysis of standards (run every fifth sample) was 8%.

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APPENDIX E

PCB CHEMISTRY DATA FOR WATER, SEDIMENT, AND FISH

APPENDIX E

PCB CHEMISTRY DATA FOR WATER, SEDIMENT, AND FISH

TABLE E.1. Concentrations (µg/L) of PCBs in Hanford Water Samples

	Location	1-Liter Water Grab	XAD-2 Samples	High-Volume Filtration Samples
	Gable Mountain Pond	<80 <20	<0.3 (42 L) ^(a) 1.9 (30 L)	0.88 ± 0.10 (2990 L) ^(b)
•	B Pond	<20 <20	1.39 (32 L) 3.75 (33 L)	
M	West Pond	<20 <20	<0.3 (48 L) 0.4 (38 L)	10.1 ± 0.86 (500 L)
postari	White Bluffs Slough (Columbia River)	<20 <20	2.76 (26 L) <0.4 (34 L)	
· ·	Wahluke Slope (unnamed pond)	<20 <20	<0.5 (24 L)	

Data in parentheses indicate volume of water sample. Results are from three replicate filters, each of which sampled 1/8 of the water sample. Results are mean ± s.d.

TABLE E.2. Concentrations (μg/kg) of PCBs in Sediments from Five Hanford Water Bodies

Location	Sample	Depth .0-5 cm	Depth 5-10 cm
Gable Mountain Pond	SG-1 ^(a)	130	(d)
	SG-2	17	
	C-3 ^(b)	8	2
	C-5	42	26
	C-7	5	4
	C-9	1	ND
B Pond	SG-1 SG-2	230 190	
	C-3	6	6
	C-5	180	220
	C-7	26	7
	C-9	28	24
West Pond	SG-1 SG-2	4 ND	
	C-3	ND	<1
	C-7	4	1
White Bluffs Slough	SG-1	ND(c)	
(Columbia River)	SG-2	ND	
	C-3	· ND	ND
	C-5	ND	ND
	C-7	ND	ND
Wahluke Slope	SG-1	ND	
(unnamed pond)	SG-2	2	
	C-5	ND	ND
	C-7	ND	ND
	C-9	ND	<1

⁽a) SG indicates a sediment grab sample.(b) C indicates a core sample. Even purel.

10 mm

⁽b) C indicates a core sample. Even-numbered core samples were not within the analysis scope of this project and are archived for potential future analysis.

⁽c) ND indicates that no concentrations were detected (detection limit ~0.1 ppb.

⁽d) Dash indicates that no sample was taken.

TABLE E.3. Concentrations ($\mu g/wet$ wt) of PCBs in Fish^(a) Collected from Aquatic Habitats on the Hanford Site

		Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	X ± s.d.
	Gable Mountain Pond						
	Liver Eggs Fat	<0.04 <0.04 2.09	0.08 <0.04 3.78	0.09 <0.04 4.40	0.05 <0.04 3.18	0.24 <0.04 2.47	<0.04 3.2 ± 0.9
		Sample #6	Sample #7	Sample #8			<u> </u>
	Wahluke Slope (unnamed pond)						
o	Liver Eggs Fat Gonads	<0.04 <0.04 <0.04 -5	<0.04 -2 -4 <0.04	<0.04 -5 <0.04 -5			<0.04 <0.04 <0.04 <0.04
		Sample #9	Sample #10	Sample #11	Sample #12	Sample #13	<u>X</u>
CAN	White Bluffs Slough (Columbia River)					iver)	
Øi. ≥ 20	Liver Eggs Fat Gonads	0.16 0.44 -4 -3	<0.04 -2 -4 <0.04	<0.04 <0.04 -4 -2	<0.04 -2 -4 <0.04	<0.39 <0.04 4.72 -6	4.72 (n=1) <0.04

Samples 1-5, Goldfish, all female Sample 6, Carp female

Sample 7, Pumpkinseed male Sample 8, Bluegill Sample 9, Smallmouth bass female

Sample 10, Smallmouth bass male Sample 11, Carp female Sample 12, Largemouth bass male

Sample 13, Carp male

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